LCAO Calculation of Dynamical Charges and Ferroelectricity

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Abstract. In this paper we discuss some of the details of the calculation of the macroscopic polarization, via the Berry-phase approach, using a general (numerical) local combination of atomic orbitals (LCAO) as a basis set. Previous implementations with a LCAO basis relied on the use of gaussian expansions, where analytical formulas exist for the crucial matrix elements. However, our approach, which only requires the matrix elements of the position operator, can be more easily implemented in the case of numerical orbitals. This work is a necessary first step towards our main goal of applying the SIESTA code to the study of ferroelectric alloys. This code, which uses a numerical LCAO basis set, has been highly optimized for the treatment of large systems. We are confident that it will allow us to treat larger systems than the standard plane-waves methods, while keeping a reasonable accuracy. Test results for representative ferroelectric perovskites are presented.

INTRODUCTION

Currently there is great interest in the study of the ferroelectric properties of different alloys, such as PZT, PMN-PT, or PZN-PT [1–3]. These alloys exhibit very large piezoelectric constants, which make them especially attractive for technological applications [1]. Unfortunately, the role of first-principles calculations in the study of these materials has been highly limited by the small system sizes that can be treated by standard methods. For methods such as plane-waves (PW), even when using ultrasoft Vanderbilt pseudopotentials [4], calculations with simulations cells containing more than a few tens atoms are a highly demanding computational task. The situation is even worse for methods such as augmented plane-waves (APW). These size limitations have forced to consider only highly ordered configurations of the alloys in the calculations performed to date [2,3,5]. It is true that even these very idealized calculations can be quite useful in determining whether the large measured pizoelectric constants are mainly due to the so-called *extrinsic* factors (movement of grain boundaries, presence of point defects, etc...), or to the *intrinsic* properties of the materials. However, calculations with more complicated ("disordered") structures are necessary to obtain more reliable theoretical estimates

predictions for the alloys, which can be compared more directly with experiments. This is especially important since a recent calculation has shown that lowering the symmetry of the simulation cell can increase the piezoelectric response [5]. Actually this is not very surprising since there is some evidence that the relaxation of the atomic positions under an applied strain is the main factor determining the piezoelectric response. Imposing a high symmetry on the supercells can prevent some kinds of atomic relaxation, yielding a smaller estimate for the piezoelectric constants.

This has been our motivation for undertaking the modifications of the SIESTA program [6] required for being able to perform calculations in ferroelectric perovskites with the desired accuracy. This program has been especially optimized to perform self-consistent density-funtional calculations for very large systems. It uses a numerical LCAO basis of finite range pseudo-atomic orbitals (PAO) [7], and also an auxiliary real-space grid to compute the Hartree and exchange-correlation contributions to the energy and forces. The computational cost (time and memory) scales linearly with the system size ($\mathcal{O}(N)$) for all the tasks, such as the construction of the self-consistent Hamiltonian or, when using the appropriate techniques [8], the diagonalization. Among the performed modifications we can cite the inclusion of semicore shells, and the corresponding use of several Kleinman-Bylander projectors for each angular momentum [9]. We have also implemented the calculation of the macroscopic polarization using the Berry-phase approach, which is necessary when standard diagonalization is used (i.e., when Bloch instead of Wannier functions are used). In the following we describe in detail our implementation of the polarization calculation, which can be easily applied to any LCAO method, and then present some examples of test calculations in perovskite oxides.

POLARIZATION CALCULATION

Only very recently has it become possible to calculate the macroscopic polarization as a bulk quantity from the electronic structure of a periodic solid, using the so-called "Berry-phase" theory of polarization [10,11]. With this powerful tool, it is possible to compute quantities like the dynamical charges [10] and piezoeletric constants [12,13] from standard first-principles calculations.

The Berry-phase approach provides a straightforward method for calculating the change in the macroscopic polarization when the system undergoes an adiabatic change from a state λ_1 to a state λ_2. The system has to remain insulating along the transformation path, and the macroscopic electric field is kept at zero. If $\mathbf{R}_i$ are the lattice vetors and $\mathbf{P}_e^{(\lambda)} = \sum_{i=1}^{3} P_e^{i\,(\lambda)} \mathbf{R}_i$ is the electronic contribution to the macroscopic polarization, then we have

$$2\pi\, P_e^{i\,(\lambda)} = \mathbf{G}_i \cdot \mathbf{P}_e^{(\lambda)} = -\frac{2e}{(2\pi)^3} \int_{BZ} d\mathbf{k}\ \mathbf{G}_i \cdot \frac{\partial}{\partial \mathbf{k}'} \psi^{(\lambda)}(\mathbf{k}, \mathbf{k}') \bigg|_{\mathbf{k}'=\mathbf{k}} \tag{1}$$

$$\psi^{(\lambda)}(\mathbf{k}, \mathbf{k}') = \mathrm{Im}\left[\ln\left(\det\langle u_{\mathbf{k}n}^{(\lambda)} | u_{\mathbf{k}'m}^{(\lambda)}\rangle\right)\right] \tag{2}$$

where $\mathbf{G}_i$ is the corresponding reciprocal lattice vector, e is the electron charge, and $u_{\mathbf{k}n}(\mathbf{r})$ is the periodic part of the Bloch function. The factor of two comes from the spin degeneracy, which we will always assume in order to simplify the notation. The quantum phase $\psi^{(\lambda)}(\mathbf{k}, \mathbf{k}')$ is defined as the imaginary part of the logarithm of the determinant of the overlap matrix between the occupied $u_{\mathbf{k}n}(\mathbf{r})$ at different points $\mathbf{k}$ and $\mathbf{k}'$. It is worth noting that the derivative of the quantum phase appearing inside the integral in (1) is not a well-defined quantity, since it depends on the particular choice of *gauge* [14]. For the computation of (1) a gauge has to be chosen such that $u_{\mathbf{k}+\mathbf{G}}^{(\lambda)}(\mathbf{r}) = e^{-i\mathbf{G}\cdot\mathbf{r}}u_{\mathbf{k}}^{(\lambda)}(\mathbf{r})$. Once this condition is imposed, the remaining gauge freedom will be reflected in the fact that the polarization is only defined modulo $2e\mathbf{R}/\Omega$ [10,13], Ω being the volume of the unit cell, and $\mathbf{R}$ a lattice vector. Usually this does not represent a problem, as the factor $2e\mathbf{R}/\Omega$ can be eliminated by inspection, and tipically one computes changes in polarization between configurations close enough so that $|\Delta\mathbf{P}| = |\mathbf{P}(\lambda_2) - \mathbf{P}(\lambda_1)| << |2e\mathbf{R}\Omega|$.

In practical calculations, the integral is replaced by a discrete summation, and a finite-difference approximation is taken for the derivative [10]: $\Delta k_i \frac{\partial}{\partial k_i'} \psi^{(\lambda)}(\mathbf{k}, \mathbf{k}')\Big|_{\mathbf{k}'=\mathbf{k}} \approx \frac{1}{2}[\psi^{(\lambda)}(\mathbf{k}, \mathbf{k}+\Delta k_i) - \psi^{(\lambda)}(\mathbf{k}, \mathbf{k}-\Delta k_i)]$. Then formula (1) becomes (particularized here for the first unit cell vector)

$$\mathbf{G}_1 \cdot \mathbf{P}_e^{(\lambda)} \approx -\frac{2e}{\Omega N_2 N_3} \sum_{i_2=0,i_3=0}^{N_2-1,N_3-1} \sum_{i_1=0}^{N_1-1} \psi^{(\lambda)}(\mathbf{k}_{i_1 i_2 i_3}, \mathbf{k}_{i_1+1 i_2 i_3}) , \tag{3}$$

where we have split the sum to stress the fact that we have a two-dimensional integral in the plane defined by $\mathbf{G}_2$ and $\mathbf{G}_3$, and a linear integral along $\mathbf{G}_1$. Due to the approximation in the derivative, the linear integral usually requires a finer mesh than the surface integral. The calculation of the quantum phase (2) between two neighboring points is therefore the only ingredient necessary to compute the polarization. We will show in the following how this can be easily done using a LCAO basis.

The expression for the Bloch functions $\Phi_{\mathbf{k}\,n}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}n}(\mathbf{r})$ using a basis of local orbitals ϕ_μ centered, within the unit cell, at the positions τ_μ is

$$\Phi_{\mathbf{k}\,n}(\mathbf{r}) = \sum_\mu^{N_b} \alpha_{\mathbf{k}\,n}^\mu \sum_i e^{i\mathbf{k}\cdot(\tau_\mu + \mathbf{R}_i)} \phi_\mu(\mathbf{r} - \tau_\mu - \mathbf{R}_i) , \tag{4}$$

where N_b is the number of basis orbitals in the unit cell, and $\mathbf{R}_i$ represent the set of all possible lattice translations. Using this definition to calculate the overlaps appearing in (2) we obtain

$$\langle u_{\mathbf{k}\,n}|u_{\mathbf{k}+\Delta\mathbf{k}\,m}\rangle = \langle \Phi_{\mathbf{k}\,n}|e^{-i\Delta\mathbf{k}\cdot\mathbf{r}}|\Phi_{\mathbf{k}+\Delta\mathbf{k}\,m}\rangle =$$

$$\sum_\nu^{N_b} \sum_\mu^{N_b} \alpha_{\mathbf{k}\,n}^{\nu\,*} \alpha_{\mathbf{k}+\Delta\mathbf{k}\,m}^\mu \sum_i e^{-i\mathbf{k}\cdot(\mathbf{R}_i + \tau_\nu - \tau_\mu)} \langle \phi_\nu(\mathbf{r} - \tau_\nu - \mathbf{R}_i)|e^{-i\Delta\mathbf{k}\cdot(\mathbf{r}-\tau_\mu)}|\phi_\mu(\mathbf{r} - \tau_\mu)\rangle . \tag{5}$$

Therefore it is necessary to calculate the matrix elements of the plane-wave with wave vector $\Delta\mathbf{k}$ between all the orbitals which have an appreciable overlap. Formulas similar to (5) have been implemented by several authors [15,16], mainly in the context of Hatree-Fock calculations. However, in those cases the use of a gaussian expansion for the orbitals simplifies considerably the calculation, as analytical formulas exist for the matrix element of a plane-wave between two gaussian functions centered on different points [15]. In our case, the numerical basis of pseudo-atomic orbitals with a finite localization radius [6,7] is not well suited for an expansion using a small number of gaussians, and we have decided to take a different route: the plane-waves appearing in equation (5) are expanded to first order $e^{-i\Delta\mathbf{k}\cdot(\mathbf{r}-\tau_\mu)} \approx 1 - i\Delta\mathbf{k}\cdot(\mathbf{r}-\tau_\mu) + \mathcal{O}(\Delta k^2)$, and then we use the matrix elements of the position operator, which are easier to calculate numerically than those of the original plane-wave. This approach follows closely the formulation proposed in the framework of empirical tight-binding [17]. It is interesting to note that, since the discretized formula (3) only holds to $\mathcal{O}(\Delta k^2)$, the approximation of the matrix elements in (5) does not introduce any further errors in the calculation of the polarization. It should also be noticed that the expansion must be made only in the last expression appearing in (5). Otherwise we find, taking into account the orthogonality between wavefuntions at different k-points, $\langle\Phi_{\mathbf{k}\,n}|e^{-i\Delta\mathbf{k}\cdot\mathbf{r}}|\Phi_{\mathbf{k}+\Delta\mathbf{k}\,m}\rangle \rightarrow -i\langle\Phi_{\mathbf{k}\,n}|\Delta\mathbf{k}\cdot\mathbf{r}|\Phi_{\mathbf{k}+\Delta\mathbf{k}\,m}\rangle$, which fails to give an approximation for $\langle u_{\mathbf{k}\,n}|\frac{\partial}{\partial\mathbf{k}}|u_{\mathbf{k}\,m}\rangle$. This failure is due to the fact that in this case $\Delta\mathbf{k}\cdot\mathbf{r}$ can be arbitrarily large, regardless of the value of $|\Delta\mathbf{k}|$, as the wave functions are defined in all space, and pairs of overlapping orbitals can be found at an arbitrarily large distance from the origin.

In the present implementation we have chosen a symmetrized version of the formulas, and the approximation to equation (5) reads

$$
\sum_{\nu}^{N_b}\sum_{\mu}^{N_b}\alpha_{\mathbf{k}\,n}^{\nu\,*}\alpha_{\mathbf{k}+\Delta\mathbf{k}\,m}^{\mu}\sum_{i}e^{i(\mathbf{k}+\frac{\Delta\mathbf{k}}{2})\cdot\mathbf{X}_{\mu\nu}^{i}}\left[\ \langle\phi_\nu(\mathbf{r})|\phi_\mu(\mathbf{r}-\mathbf{X}_{\mu\nu}^{i})\rangle\right.
$$
$$
\left. -i\frac{\Delta\mathbf{k}}{2}\cdot\left(\langle\phi_\nu(\mathbf{r})|\ \mathbf{r}\ |\phi_\mu(\mathbf{r}-\mathbf{X}_{\mu\nu}^{i})\rangle + \langle\phi_\nu(\mathbf{r}+\mathbf{X}_{\mu\nu}^{i})|\ \mathbf{r}\ |\phi_\mu(\mathbf{r})\rangle\right)\ \right], \tag{6}
$$

where $\mathbf{X}_{\mu\nu}^{i} = \tau_\mu + \mathbf{R}_i - \tau_\nu$. At first sight it may seem surprising that in the evaluation of the matrix elements of the position operator in (6), the origin is alternately taken on each atom, rather than using a common one. Actually it can be easily shown that the origin can be arbitrarily shifted to any point $\mathbf{t}_0$, if the appropriate compensating phase factor $e^{i\Delta\mathbf{k}\cdot\mathbf{t}_0}$ is introduced. To first order in $|\Delta\mathbf{k}|$ all the choices should give the same result.

We will now briefly comment on the calculation of the matrix elements. Our basis orbitals can be expressed as a product of a radial function with the corresponding spherical harmonic, $\phi_\nu^{l_\nu m_\nu}(\mathbf{r}) = \phi_\nu(r)Y_{l_\nu m_\nu}(\hat{\mathbf{r}})$. The overlap matrix between two of those orbitals is then easily calculated using their Fourier transforms, $\tilde{\phi}_\nu^{l_\nu m_\nu}(\mathbf{q}) = \tilde{\phi}_\nu(q)Y_{l_\nu m_\nu}(\hat{\mathbf{q}})$, where $\tilde{\phi}_\nu(q) = \frac{i^l}{2\pi^2}\int dr\ r^2\ j_l(qr)\ \phi_\nu(r)$, and $j_l(x)$ are the spherical

Bessel functions. This is advantageous and has been used in the SIESTA code [6], with the overlap given by

$$\langle \phi_\nu^{l_\nu m_\nu}(\mathbf{r}) | \phi_\mu^{l_\mu m_\mu}(\mathbf{r} - \mathbf{R}_{\mu\nu}) \rangle = \sum_{lm} S_{\nu\mu}^l(R_{\mu\nu}) \, G(l_\nu, m_\nu; l_\mu, m_\mu, l, m) \, Y_{lm}(\hat{\mathbf{R}}_{\mu\nu}), \quad (7)$$

where

$$S_{\nu\mu}^l(R_{\mu\nu}) = 4\pi \imath^l \int dq \; q^2 \; j_l(qR_{\mu\nu}) \, \tilde{\phi}_\nu^*(q) \, \tilde{\phi}_\mu(q). \quad (8)$$

The sum in l and m has very few terms, as the coefficients $G(l_\nu, m_\nu; l_\mu, m_\mu, l, m) = \int d\Omega \; Y_{l_\nu m_\nu}^*(\hat{\mathbf{r}}) \, Y_{l_\mu m_\mu}(\hat{\mathbf{r}}) \, Y_{lm}^*(\hat{\mathbf{r}})$ are non-zero only when $|l_\nu - l_\mu| < l < l_\nu + l_\mu$, the sum of all the angular momenta $l_\nu + l_\mu + l$ is an even number, and $m_\mu - m_\nu - m = 0$. Therefore, in order to calculate the matrix elements of the position operator appearing in (6) we only need the Fourier transform of $\mathbf{r}\phi_\nu^{l_\nu m_\nu}(\mathbf{r})$. This can be easily computed using expressions of the type,

$$(\tilde{z\phi})_\nu^{l_\nu m_\nu}(\mathbf{q}) = \sqrt{\frac{4\pi}{3}} [\; F_\nu^{l_\nu+1}(q) \; G(1, 0; l_\nu, m_\nu; l_\nu + 1, m_\nu) \; Y_{l_\nu+1 \, m_\nu}(\hat{\mathbf{q}}) +$$
$$F_\nu^{l_\nu-1}(q) \; G(1, 0; l_\nu, m_\nu; l_\nu - 1, m_\nu) \; Y_{l_\nu-1 \, m_\nu}(\hat{\mathbf{q}}) \;], \quad (9)$$

where

$$F_\nu^L(q) = \frac{\imath^L}{2\pi^2} \int dr \; r^3 \; \phi_\nu(r) \; j_l(qr), \quad (10)$$

and z is the quantization direction of the angular momentum. Similar formulas, involving also $F_\nu^{l_\nu+1}(q)$ and $F_\nu^{l_\nu-1}(q)$, can be written for $(\tilde{x\phi})_\nu(\mathbf{q})$, and $(\tilde{y\phi})_\nu(\mathbf{q})$. Therefore, it is evident that the calculation of the matrix elements of the position operator is not any more difficult than the calculation of the overlap matrix, as it involves the same kind of operations. In practical calculations, the expansion of $\mathbf{r}\phi_\nu^{l_\nu m_\nu}(\mathbf{r})$ in spherical harmonics, and the calculation of the coefficients $G(l, m; l', m'; l'', m'')$ have been done numerically using Gauss-Legendre quadrature integration [18].

RESULTS

In this section we present some results for the ferroelectric distorsion and dynamical charges of $BaTiO_3$ and $PbTiO_3$ obtained with the SIESTA [6] code, using the method described above in the calculation of the dynamical charges. Before presenting the results we will comment on some of the technical details.

A double-ζ polarized basis of PAO's [6,19] has been used for all the elements. The semicore states $3s$ and $3p$ of Ti, and the $5s$ and $5p$ states of Ba have been explicitly included in the calculation. Inner states have been removed using Troullier-Martins [20] pseudopotentials generated from the configurations $3s^2 3p^6 3d^2$ for Ti,

$2s^2 2p^{3.8} 3d^{0.2}$ for O, $5s^2 5p^6$ for Ba, and $6s^2 6p^2$ for Pb. The pseudopotentials were put into a separable form [9], and two different projectors were used for those angular momenta where a semicore shell was included in addition to the valence states. In those cases the projectors were constructed from the pseudo-atomic wavefunctions and orthogonalized following the prescription by Blöchl [9].

The Perdew-Zunger parametrization of the Ceperly-Alder exchange-correlation potential [21] was used. The Brillouin zone was sampled with a $6 \times 6 \times 6$ Monkhrost-Pack [22] grid in all the self-consistent calculations, while a $4 \times 4 \times 20$ integration grid was used in the calculation of the polarization. The spacing of the real-space mesh used to calculate the Hartree and exchange-correlation contributions to the forces and energies [6] was equivalent to a 200 Ry plane-wave expansion. Once self-consistency was achieved, the calculated density matrix was used to average forces and energies over two different meshes (shifted relative to the atoms). This has an effect similar to the use a much higher cut-off, effectively improving the convergence of the results. With the use of this scheme total energies are converged within a few meV, even with the highly localized semicore states present in these systems.

For cubic $BaTiO_3$ and $PbTiO_3$ we obtain equilibrium lattice constants of 7.44 and 7.26 Bohr, and bulk moduli of 213 and 236 GPa respectively. For the Ba compound this data compare quite well with other local density (LDA) calculations, which give lattice parameters of 7.45 [23,24] and 7.46 Bohr [25], and a bulk modulus of 196 GPa [25], while the experimental lattice constant is approximately 2 % larger, a_0=7.56 Bohr. The agreement is somewhat less satisfactory in the case of $PbTiO_3$, for which the published LDA results are 7.34-7.35 Bohr for the lattice constant, and 203-215 GPa for the bulk modulus [25,26]. The experimental lattice constant in the cubic phase is 7.50 Bohr.

Table 1 shows the frequency and eigenvector of the soft modes at the theoretical and experimental equilibrium volumes. In this table O_I refers to the oxygen atom which moves along the Ti-O bond, while O_{II} refers to the two oxygen atoms moving perpendicularly to this bond. The dynamical matrix at Γ was calculated by finite differences from the forces acting on the atoms in the unit cell when they are displaced by $0.005a_0$ from their ideal positions in the cubic structure. The results for the eigenvectors are in quite good agreement with the recent calculation of Ref. [23] using PW and density functional perturbation theory. In particular, our

TABLE 1. Soft mode eigenvector (in real space) and frequency at Γ point.

		a_0 (a.u.)	ω (cm^{-1})	Ba/Pb	Ti	O_{II}	O_I
$BaTiO_3$	SIESTA	7.45	i199	-0.000	-0.102	0.070	0.148
	SIESTA	7.56	i310	-0.000	-0.093	0.061	0.171
	PW [23]	7.56	i219	-0.002	-0.096	0.071	0.158
	APW [24]	7.56	i72	-0.001	-0.091	0.090	0.145
$PbTiO_3$	SIESTA	7.26	i98	-0.027	-0.003	0.147	0.099
	SIESTA	7.50	i249	-0.011	-0.077	0.099	0.153
	PW [23]	7.50	i180	-0.016	-0.058	0.120	0.143

TABLE 2. Dynamical charges of cubic $BaTiO_3$ and $PbTiO_3$, calculated at the experimental lattice parameter (respectively 7.56 and 7.50 Bohr)

	$BaTiO_3$			$PbTiO_3$		
	SIESTA	PW [23]	PW [27]	SIESTA	PW [23]	PW [27]
$Z_A^\star$	+2.72	+2.74	+2.75	+3.96	+3.87	+3.90
$Z_{Ti}^\star$	+7.60	+7.32	+7.16	+7.40	+7.04	+7.06
$Z_{O_{II}}^\star$	-2.18	-2.14	-2.11	-2.65	-2.57	-2.56
$Z_{O_I}^\star$	-5.96	-5.78	-5.69	-6.06	-5.76	-5.83

data reproduces the different character of the ferroelectric distorsion in $BaTiO_3$ and $PbTiO_3$. While in the former the distorsion is dominated by the displacement of Ti against O along the Ti-O chains, in the latter it also has an appreciable component arising from the motion of the Pb atoms against the oxygen atoms in the Pb-O planes [23]. At the experimental volumes, the frequencies of the soft modes are 30%-40% larger in our case than those reported in Ref. [23]. This may indicate an overestimation, at least at these volumes, of the depth of the potential wells compared to the PW results.

Table 2 shows a comparison between the dynamical charges calculated with the present method and with PW [23,27]. The overall agreement is good. The anomalous Born effective charges of Ti and O_I are well reproduced, but their values are around 5% larger in our LCAO calculation than in the PW ones. These discrepancies may be attributed to the different basis set, and not to the details of the method used in the computation of the dynamical charges. At the present time very few calculations of dynamical charges are available where a LCAO basis set is used in combination with LDA, and therefore it is not possible to establish any general trends. However, it is worth to notice that in the calculation reported in Ref. [28], where a gaussian basis set was used to compute the properties of $KNbO_3$, the values of the anomalous effective charges for Nb and O_I were overestimated by 7% and 15% respectively, compared to PW-based calculations. In that case the authors attributed the differences to the fact that the basis set was optimized for Hartree-Fock calculations, rather than LDA.

Results for the dynamical charge $Z_{33}^\star$ in tetragonal $PbTiO_3$ are shown in Table 3. Our calculation has been performed at the experimental structure [12]. The values taken from Ref. [2] were calculated at the fully optimized structure, while in Ref. [12]

TABLE 3. Dynamical effective charge $Z_{33}^\star$ in tetragonal $PbTiO_3$.

$Z_{33}^\star$	SIESTA	LAPW [12]	PW [2]
Pb	4.02	3.52	3.5
Ti	4.61	5.18	5.5
O_{II}	-2.18	-2.16	-2.2
O_I	-4.27	-4.38	-4.6

TABLE 4. Band-by-band decomposition of the dynamical charges of Ti and O_I in cubic $BaTiO_3$ with a_0=7.45 a.u.

	$Z^\star_{Ti}$		$Z^\star_{O_I}$	
	SIESTA	PW [29]	SIESTA	PW [29]
Ti $3s$	-2.06	-2.03	0.04	0.02
Ti $3p$	-6.20	-6.22	0.21	0.21
Ba $5s$	0.06	0.05	0.01	0.01
O $2s$	0.29	0.23	-2.58	-2.51
Ba $5p$	0.37	0.36	-0.12	-0.13
O $2p$	3.17	2.86	-9.66	-9.31
Core	12.00	12.00	6.00	6.00
Total	7.63	7.25	-6.10	-5.71

the experimental unit cell volumen was preserved during the energy minimization. The different choices of the reference structure are probably behind some of the differences in the data presented in Table 3. However, all the calculations seem to agree in the large reduction of Ti and O_I effective charges when going from the cubic to the tetragonal phase. Our approach also succeed in reproducing this behaviour.

Some insight into the origin of the small discrepancies shown in Table 2 can be obtained by performing a decomposition of the dynamical charges into contributions coming from different isolated groups of bands. This is usually known as a band-by-band decomposition. Table 4 shows the results for Ti and O_I in cubic $BaTiO_3$, compared with those published in Ref. [29]. For both $Z^\star_{Ti}$ and $Z^\star_{O_I}$ we perfectly reproduce the anomalous contribution coming from Ti 3p (-0.20, +0.21), O 2s (+0.29, -0.58), and Ba 5p (+0.37, -0.12). However, the contribution from the O 2p group of bands is 11% (Ti) and 4% (O_I) larger in the LCAO case. This seems to indicate that the hybridization between Ti 3d and O 2p is not fully reproduced by our LCAO basis set, with a stronger effect on the Ti effective charge. The inclusion of more diffuse d polarization orbitals on the O atoms, or even a shell of quite extended f polarization orbitals on Ti, only reduces the computed dynamical charges by very small amounts (of the order of 1%).

CONCLUSIONS

In this paper we have presented an implementation of the calculation of the macroscopic polarization, by means of the Berry-phase approach, using a LCAO basis set. The usual discretized Berry-phase formula is expressed in terms of the matrix elements of the position operator in the basis orbitals. These matrix elements are much easier to calculate using a numerical basis than those of a plane-wave, required in the previous implementations. Our method has been coded, along with other necessary modifications for a reliable treatment of the ferroelectric oxides,

within the SIESTA program. This code performs self-consistent LDA calculations using a flexible LCAO basis set of numerical orbitals, and allows for the treatment of very large systems, thanks to the linear scaling of the computational cost with the number of atoms.

We have presented several test caculations for $BaTiO_3$ and $PbTiO_3$ which demostrate not only the uselfulness of our implementation of the polarization calculation, but also the fact that LCAO calculation can reproduce the PW results, giving a very reasonable description of these sytems. We are confident that, with the use of this LCAO method, we will be able to increase the size of the systems that can be treated with *ab initio* methods, allowing for a more realistic simulation of the properties of the complex ferroelectric oxides.

ACKNOWLEDGMENTS

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